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pH Sensing at Pt Electrode Surfaces Coated with Linear Polyethylenimine from Anodic Polymerization of Ethylenediamine

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A novel pH sensor using a smooth Pt electrode coated with an electrically insulating polymer is addressed in this study. We present a new electrochemically modified Pt electrode. Its modification results from the anodic oxidation of pure ethylenediamine, charged with lithium trifluoromethanesulfonate, which leads to the formation of a polymer coating in one step. The assembly of the electrode surface coated with electropolymerized ethylenediamine acts as a transducer of the electrode potential *vs.* the pH value in aqueous solutions. It has been shown that the anodic oxidation of pure ethylenediamine yields polyethylenimine which is a high impedance polymer containing amino groups sensitive to H^+ concentration. Since the reproducibility of polymer-based pH sensors is a controversial subject, we examined both the effect of the electrode-bias time, which can be linked to the polymer thickness, and the aging of the polymer on the potentiometric response of the sensor. The pH sensor we propose here has a quasi-Nernstian behavior. It is reliable for some weeks in the pH range from 3 to 11 in aqueous media.
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pH measurements are performed a countless number of times every day, in all pH dependant chemical processes, especially in crucial areas such as agribusiness, the pharmaceutical industry, and human health. Despite the importance of monitoring accurately the pH changes in a medium, there are not many ways to control the acidity (or basicity). Electropolymerization is a widely used technique for the fabrication of chemical and biochemical sensors. The resulting passivating films fulfill a great number of roles. Chemical sensing, enzyme immobilization,[1] and molecule grafting[2] are the more common applications. Electrochemically modified electrodes with electroactive polymers were proposed as a substitute for the pH glass electrode. Recently it has been shown that electromodified electrodes with conducting polymers could act as good candidates for replacement of popular glass pH electrodes.[3] So far all pH chemical sensors using polymer-film-coated electrodes were made from the electropolymerization of pyrrole,[4] aniline,[5] thiophene, or benzene derivatives.[6-9] With these conductive polymers, measurements are not very reliable due to the random nature of the deposition process. Polymers grown under identical conditions may have different remittances to interferents due to film defects and pinholes.[10] It is even necessary to overoxidize the layer of the conductive polymer to protect it from strong oxidizing agents or high anodic potentials as is the case for polypyrrole, which modifies its electrical properties drastically.[11,12]

With the resulting nonconductive polymers, the films coated on the electrode surface have a uniform thickness and grow thick enough to become insulators with fewer defects and pinholes. Compared to conductive polymers, nonconductive polymers usually have a high selective response and a high impedance, which is important for eliminating interference by other electroactive species.[13,14]

Consequently, our research focused on obtaining an insulating polymer whose surface was covered with -NH_2 groups. This was recently achieved. We reported the possibility of electropolymerizing ethylenediamine (EDA), a primary diamine, and yielding polyalkylimines.[15] The electrochemical behavior of EDA, for example, in solution in acetonitrile at a carbon fiber, leads to a monolayer of oxidized EDA molecules bonded to the electrode by both nitrogen atoms.[16] By contrast, we found that it was possible to polymerize EDA or diethylenetriamine (DETA) by anodization. The crux of this finding was the use of pure liquid diamines, charged with a salt, to obtain an electrolyte. The mechanism of this polymerization has been described.[17] Consequently, diamines, which are neither conjugated nor aromatic, can evolve into a strong, adhesive, insulating coating on the electrode. This coating consists of an alkylimine polymer, here linear polyethylenimine[17] (L-PEI) which is an insulating polymer.

In this case, the resistance of this polymer was estimated by frequency response impedance measurement: the resistivity value is about 20 MΩ/cm after prior preparation of the coating with a 1 h bias at +3 V. 1,3-diaminopropane (1,3-DAP) gives linear polypropylenimine (L-PPI). Diethylenetriamine (DETA) yields L-PEI, too. These polymers, when grafted on electrodes, are insoluble in various common solvents, and durably modify the electrochemical behavior of the electrode. The electropolymerization of diamines occurs on different metallic, nonmetallic, or semiconducting material electrodes, such as smooth gold, smooth platinum, glassy carbon, p- or n-type silicon, and fluorine tin oxide (FTO).[5,17]

A novel class of pH electrodes is presented here, resulting from coating the electrode by anodic oxidation of ethylenediamine-based electrolytes. Smooth Pt electrodes, coated with L-PEI thin films, formed on the platinum surface, act as transducers. The principle is based on the reliable and sensitive potentiometric response of the electrode as a function of the pH changes and is due to the numerous surface amino groups in equilibrium with the protons in solution.

Experimental

Materials.—EDA, branched polyethylenimine (B-PEI) and lithium trifluoromethanesulfonate (lithium triflate) were from Sigma-Aldrich, and were used in a glove box (Jacomex, France) as received under an Ar stream of electronic grade (Argon U, Air Liquide, France). Buffered solutions, Titrinorm grade according to National Institute of Standards and Technology (NIST), were from Prolabo, France, and were stored at +4°C.

Apparatus.—All cyclic voltammetry and frequency response analysis (FRA) experiments were performed using an autolab, model PGSTAT 20 (Ecochemie, The Netherlands), controlled by a PC computer via a GPES software interface. The electrochemical cell consisted of a classic three-electrode setting with an Ag wire as the reference electrode (noted SRE for silver reference electrode), a platinum disk as the counter electrode and a smooth platinum disk electrode (0.785 mm^2 area) as the working electrode. The electrochemical quartz crystal microbalance (EQCM) from Maxtek-USA, model PM 710 using AT-cut 5 MHz platinum-plated quartz as the working electrode (1.37 cm^2), was coupled to cyclic voltammetry measurements. Electrode potential in the different buffered solutions were measured *vs.* a saturated calomel electrode (SCE), XR100 model from Radiometer Analytical-France, via a pH meter,

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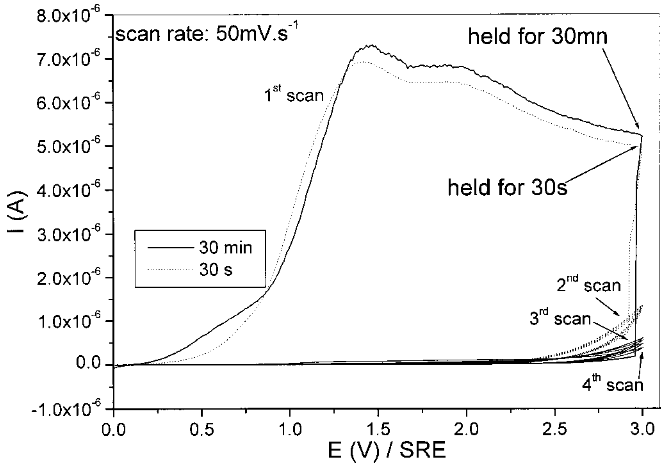

Figure 1. Cyclic voltammograms of 0.01 M $LiCF_3SO_3$ in pure EDA at a smooth platinum electrode for two bias times, 30 s and 30 min. The curve for 1 h is very closed to that for 30 min.

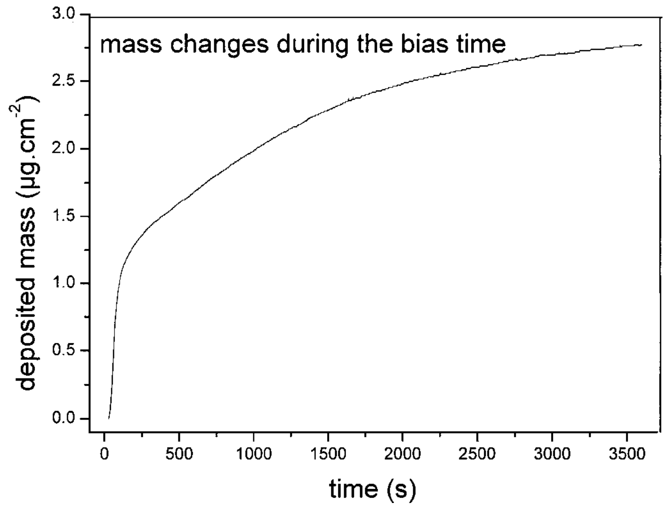

Figure 2. Mass changes at the electrode surface *vs.* elapsed time.

PHN130T model (Tacussel Electronics, France), used as a high impedance voltmeter (>10 MΩ). Consequently, each potentiometric measurement was performed with an accuracy of ±1 mV.

The surface profilometer apparatus we used was an Alpha-step 100 profilometer (KLA-Tencor, USA) with digital interface readout and a strip charge recorder with a resolution of 50 Å.

Electrode treatment methods.—Given the numerous electropolymerization protocols, which exist (due to the vast variety of electropolymerizable monomers), we developed our own protocol.

Before each anodic passivation, all electrodes were polished with alumina (particle size 1 µm) and rinsed with pure water. The L-PEI films were electrodeposited onto the smooth Pt surface by means of cyclic voltammetry in 0.01 mol/L lithium triflate solutions of pure ethylenediamine. Five cycles between 0 and 3 V *vs.* SRE at 50 mV/s were performed, and during the first scan the electrode was biased at 3 V for different times (0, 5, 30, or 60 min). The following four scans were performed to check the stability and the insulating property of the coating. Then the modified electrodes were rinsed in water and acetone, dried in an oven at 40°C, and tested in several buffered solutions at different pH values.

Results and Discussion

Influence of the bias time on the electrode surface.—The electropolymerization of ethylenediamine occurs as soon as the potential is higher than 2 V *vs.* SRE. This is the reason why several smooth platinum electrodes were biased at +3 V *vs.* SRE, at the end of the first scan, from 0 to 3 V, using the hold mode of the potentiostat, for different durations of bias times at +3 V, 30 s, 30 min, and 1 h. These experiments were made in order to determine the bias time for which the potentiometric electrode response *vs.* the pH is more important and reliable. After the bias at +3 V, four scans were recorded, from 0 to +3 V, to check the stability and the insulating property of the coating. From the resulting voltammograms (see Fig. 1) it appears the longer the electrode bias time is, the more the current drops. This points out the electrical insulating property of this polymer.

The mass of electrodeposited L-PEI, determined by electrochemical quartz crystal microbalance coupled to cyclic voltammetry (Fig. 2), can be linked to the bias time t. The EQCM measurements allowed us to monitor the polymer mass (through the crystal frequency) *vs.* the elapsed time or *vs.* the potential applied to the working electrode. For bias duration larger than 1 h no more beneficial effect was observed. Moreover, we have measured, with the help of a long-scan profiler apparatus, the thickness of the polymeric film deposited on electrodes held at +3 V/SRE for 0, 5, 30, and 60 min, and we obtained 2.1, 2.5, 3.8, and 4.2 µm, respectively.

pH dependence of the measured potential.—The potentiometric responses of the different biased electrodes, after immersion into buffered solutions at different pH values, are gathered in Fig. 3. In the inset are given the results of the electrode potentials measured with different electrodes made with different bias times at the end of the first scan. In all cases the electrodes were immersed 3 min into the solution and the equilibrium response time was less than 15 s. It is evident that the potentiometric response to pH changes of the solution is linear in the range from 3 to 11, but the exact mechanism by which the linear polyethylenimine responds to pH changes has not yet been elucidated. A possible explanation could be the affinity of the numerous amino groups to the protons in solution. The reaction of H^+ with amino groups creates a local charge density excess at the electrode surface. The potentiometric response can be considered as a behavior controlled by a surface reaction. Surface reactions seem to take place on the PEI film that are essentially protonation and deprotonation of superficial amino groups of the PEI as symbolically described by Eq. 1

$$PEI + H^+ \rightarrow PEIH^+ \quad [1]$$

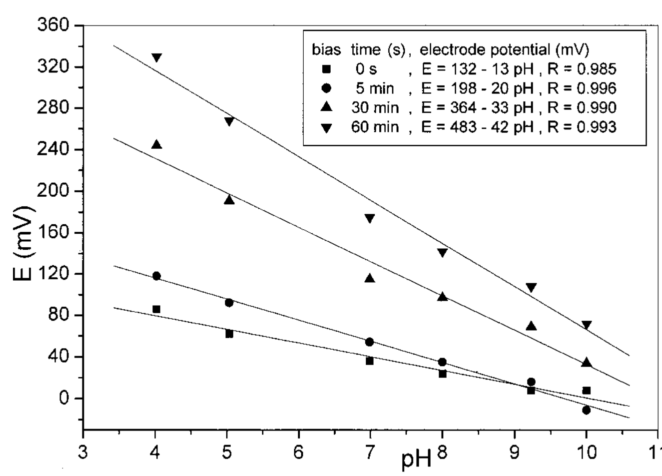

Figure 3. Potentiometric response *vs.* the pH of modified electrodes at different bias times.

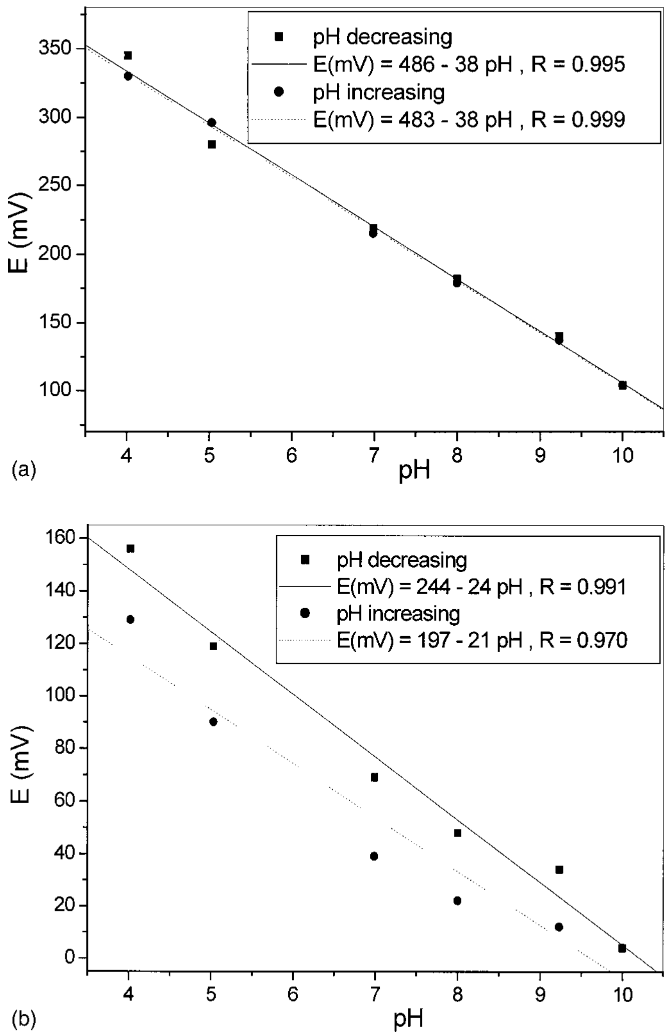

Figure 4. (a, top) Potentiometric response of PEI film electrodes *vs.* the pH changes as a function of measurement direction for the thickest PEI film. (b, bottom) Potentiometric response of PEI film electrodes *vs.* the pH changes as a function of measurement direction for the thinner PEI film.

When equilibrium is reached at the PEI/solution interface, we can write the equilibrium expression K of the surface Reaction 1 and the equilibrium potential E as follows (Eq. 2 and 3)

$$K = [\mathrm{PEIH}^+]/([\mathrm{PEI}][\mathrm{H}^+]) \qquad [2]$$

$$\begin{aligned} E &= E^o + (RT/F)\ \ln([\mathrm{PEIH}^+]/[\mathrm{PEI}]) \\ &= E^{o\prime} + (RT/F)\ \ln[\mathrm{H}^+] \end{aligned} \qquad [3]$$

According to this mechanism of reaction, we expect a potentiometric response of 59 mV/pH unit. But our electrodes showed a lower response slope than this theoretical one. The L-PEI-based pH sensors with bias time larger than 30 min at +3 V *vs.* Ag^+/Ag show nearly ideal Nerstian (−42 mV/pH) behavior in the pH range 3-11. The presence of anionic and cationic responses of the PEI film electrodes, due to the electrolyte $LiCF_3SO_3$, probably caused this difference of response slope.

We think that the more the thickness increases, the more amino groups are present, and the more the modified electrode is pH sensitive. Indeed the slope decreases from −13 (for bare electrodes) to −42 mV/pH (for electrodes biased at 3 V for 60 min) and stabilizes around this latter value. Linear regressions were also gathered in the inset of Fig. 3, and the resulting correlation factors R, close to 1, highlight a well-behaved potentiometric response to pH changes for these polyethylenimine-based thin films.

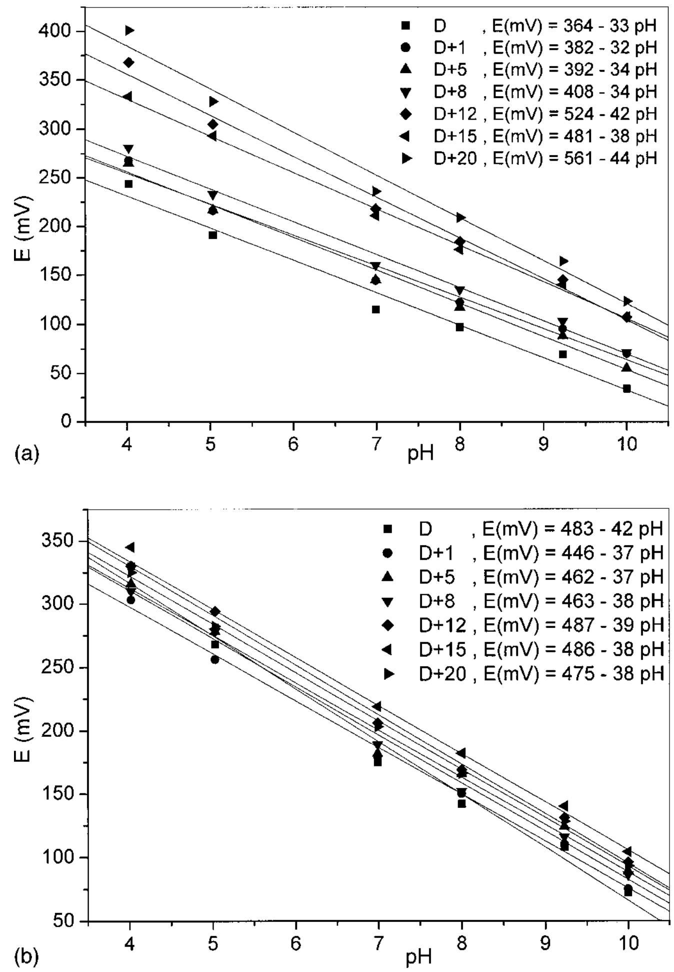

Figure 5. (a, top) Potentiometric response *vs.* the pH after aging of the electrodes modified for a bias time of 30 min at +3 V. (b, bottom) Potentiometric response *vs.* the pH after aging of the electrodes modified for a bias time of 60 min at +3 V.

Figure 4a and b show the potentiometric responses of modified electrodes 15 days after the deposition of the L-PEI films on the platinum electrodes for two different thicknesses when the measurements were conducted for increasing and decreasing pH. Good linearity and good reversibility in potentiometric measurements were observed for the electrode with a bias time of 1 h (Fig. 4a) but not for the one with any bias time (Fig. 4b) which gives a hysteresis. So only thick-film modified electrodes gave potentiometric responses that did not show a significant dependence on the direction of pH changes. Moreover, we noticed experimentally that the same potentiometric response is also obtained when the pH values vary in a random manner.

Thus we proved in this section that electrodes biased at 3 V for more than 30 min exhibit linear and reversible potential responses to pH changes. Consequently, they are good pH sensors.

Influence of aging time on the electrochemical electrode behavior.—The electrochemical behavior of the L-PEI modified electrode was examined over a period of 20 days. As the electrode was aged over 20 days, the potentiometric response to pH remained roughly the same, in particular for the electrode modified at +3 V for a bias time of 30 min (Fig. 5a) 1 h (Fig. 5b). For the latter, the slope between the second day and the twentieth day varied in the range of −37 to −39 mV/pH. So the coating is quite stable, does not evolve or decompose with time, and the potential measurements of our polyethylenimine modified electrodes are reliable.

Comparison of our L-PEI coated electrode with other PEI-modified electrodes.—Recently, a modified electrode coated with commercial branched polythylenimine (B-PEI), was proposed.[18,19] The coating needed the B-PEI to react with a cross-linker. It was charged with $Fe(CN)_6^{3-/4-}$. The system exhibited a stable potential ±10 mV), but the coating stability was limited in time because of the solubility of B-PEI in water as in common organic solvents. Other polyethylenimines exist. An organic route can synthesize L-PEI.[20] In our case, the anodic polymerization of EDA yields L-PEI, too. The solubility of L-PEI after its grafting seems very poor in water, as shown by our stability tests. Consequently our coating process, which is made easily and quickly in one step and whose thickness can be controlled, is an improvement in PEI grafting.[21]

Conclusion

Platinum electrodes, modified by a coating of a thin linear polyethylenimine film, resulting from the anodic oxidation of pure ethylenediamine exhibit a potential response sensitive to pH changes in aqueous media. This response is linear, reversible, and stable in time. Moreover, the electrodes biased 1 h at +3 V are not affected by the direction of the pH change in comparison to bare or electrodes biased less than 30 min at +3 V. From these results we propose this polymer (L-PEI) to be used in miniaturized analytical sensors. These pH measurements through the use of thin L-PEI film-coated electrodes are a part of the possible applications described in our recent patent.[21] The L-PEI films investigated here can be of great benefit in biosensor construction through the possibility of immobilizing biological molecules or redox centers in or on the film surface. Results will be reported in a forthcoming paper.

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